

## IV.C.5-Mechanistic Modeling Framework for Predicting Extreme Battery Response (SNL)

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Projected End Date: September 2015

- Implement partially saturated porous flow and solid mechanics modeling within 1DElectrode.
- Develop consistent thermodynamic/transport models of the entire cell using CANTERA. Add partial saturation and solid mechanics models to CAEBAT. Build SEI Models that can predict the autocatalytic temperature behavior experimentally observed
- Implement upscaling ideas from microstructure models within CAEBAT using both averaged results and perhaps statistical distributions.
- Exercise new capability by developing new models for thermal runaway processes with 1DElectrode / CAEBAT

### Accomplishments

- Linked 1DElectrode model into CAEBAT architecture, running thermal and electrical simulations using AMPERES/1DElectrode.
- Validated models against Dualfoil model within 1DElectrode/CAEBAT.
- 1DElectrode model improvements include real thermodynamics based chemistry (activities, ...), Stefan-Maxwell nondilute diffusion, and conservative enthalpy-based, multi-species energy conservation. This is new to battery modeling software.
- 1DElectrode model improvements include single-ion entropies and realistic electron entropies based on Seebeck coefficients. Combined, these additions allow for the correct treatment of distributed heat transfer in electrochemical systems when the thermal field is resolved across the battery.
- A formulation for the calculation of the solid-phase global stress and strain field has been written up and implemented. The change in the particle stress-free strains of the electrodes are partitioned between changing the porosity and between incorporated into the global stress-free strain field via a constitutive model. Testing is under way.
- A formulation for two-phase, multispecies electrochemical transport in porous electrodes has been developed, for subsequent implementation into 1DElectrode. This has not been completed yet.
- Successfully reconstructed 3D microscale digital models of Li-ion cathodes from FIB-SEM

### Objectives

- Address root cause and implications of thermal runaway of Li-ion batteries by delivering a software architecture solution that can lead to the development of predictive mechanisms that are based on identification of species.

### Technical Barriers

Key technical risks associated with the proposal involve the lack of mechanistic understanding of interfacial layers associated with electrodes in the Li-ion system.

Additionally barriers involving the development of mechanistic understanding of degradation mechanisms and detailed kinetics of solid phase processes and liquid phase secondary reactions abound with the Li-ion battery community. We are developing software for these mechanisms to be addressed and then are making the software available as open source. Future collaborations using the software we hope will help to fill these gaps.

Additionally we have pursued upscaling of microstructure parameters to the macrohomogeneous scale. This approach addresses some of the uncertainty.

### Technical Targets

- Implement 1DElectrode capability within CAEBAT and verify.

images and developed electrochemical transport models with Faradaic and Ohmic internal heat generation.

- Successfully simulated a 1C discharge rate in a cathode using the reconstructed 3D microscale model showing reasonable cell potential and Joule heating curves over full discharge cycle.

## Introduction

We are expanding the functionality of the CAEBAT-I architecture developed at Oak Ridge National Laboratory by incorporating advanced speciation models. These models are built on the Cantera open-source software library for elementary thermodynamic, transport and kinetic processes. We will be implementing this modeling capability to address two key aspects of Li-Ion battery chemistry that will support the existing CAEBAT-I program.

1) Modeling the processes that transform chemical energy to thermal energy in abusive scenarios and the associated heat release for both normal operation and abusive conditions. In doing this we focus on interactions between electrode-particle scale physics present within our Cantera-based approach and the cell-level physics already present within the CAEBAT framework. In follow on work, we will add models that can capture the autocatalytic temperature rise observed at elevated temperatures, fitting data from Sandia's BATLab program.

2) Modeling thermo-electro-mechanical interactions within porous materials that determine the heat, mass and electrical transport processes, addressing cell-level structural evolution under normal operation and abusive conditions. This includes modeling gasification mechanisms by adding partial saturated flow to battery models so that mechanisms for gasification may be envisioned and applied in at least a 1D context.

Our modular approach emphasizes hierarchical approaches to modeling the detailed chemistry system and onset of thermal abuse from a species-specific point of view. These represent a natural extension to the current CAEBAT architecture currently developed at ORNL. We also develop upscaling algorithms to bring information from subgrid variations in microstructure developed by Prof. Bob Kee at the Colorado School of Mines to the macrohomogeneous scale. This approach to incorporating detailed chemistry and fundamental processes into the CAEBAT OAS is based on the open-source program Cantera. Our first goal is to advance the state of the art in modeling chemical processes within the battery community using open software standards. Because the battery community has lacked such an infrastructure, fundamental quantitative comparisons of chemistry have not occurred to a significant extent within the community. We expect to emulate what has occurred within the combustion community with programs such as Chemkin, which brought together experimentalists and computational scientists to create an infrastructure, which

was then used to quantitatively understand and predict mechanistic details.

## Approach

We have had two complimentary goals within this project. The first goal is to advance the state of the art in modeling chemical processes within the battery community using open software standards. This is an important and often misunderstood goal. Because the battery community has lacked such an infrastructure, fundamental quantitative comparisons of chemistry have not occurred to a significant extent within the community. *We hope to emulate what has occurred within the combustion community with programs such as Chemkin, which brought together experimentalists and computational scientists to create an infrastructure which was then used to elucidate mechanistic details.*

The second goal of the project has been to start populating this infrastructure with models of various levels of fidelity that may address the thermal runaway process observed to occur within Li-ion batteries. Ideally this would involve understanding the formation of the SEI layer and its evolution as a function of temperature. Although the mechanistic details of this process as well as inputs for constitutive models that would make a model for this just are not available for engineering-level capabilities. We have proposed starting with those models and then work to refine them using the experimental data from Sandia's BATLab program to interpret the thermal runaway process from an engineering perspective. Furthermore, we expand the engineering details into more sophisticated level that will track individual species in mechanisms that closely resembles the corrosion processes based on our current understanding of the stability of the passivating layers. This would necessarily involve determining the stability and thermodynamics of components of the SEI layer as a function of temperature and pressure.

An unappreciated feature of batteries is the need to understand the thermo-mechanical interactions of the porous materials as a function of the state of discharge and as a function of the number of cycles. We at Sandia have started to address this issue within our codes and would like to transfer some of the technology to the CAEBAT architecture with collaboration from ORNL. This involves solving the partially saturated flow equations, which are important for some battery systems, and represent failure mechanisms in others. And we had also proposed to include the poroelastic stress constitutive equations using the effective stress principles. This concept is essentially new to batteries, though we have extensively used it in other contexts with Sandia codes such as Goma, which can model the mechanical environments found in drying porous media or porous media in contact with continuum fluids that undergo external stresses.

The impact of this project will eventually be far-reaching as the technology is deseminated into the battery community. During this project, we have created infrastructure for the inclusion of detailed mechanistic

models for thermochemical processes that are important to battery performance and safety. Additionally, the infrastructure for mechanistic understanding of thermal runaway processes in Li-ion batteries has been advanced. This capability can be linked to existing cell, module and pack-level capabilities being developed under CAEBAT-I.

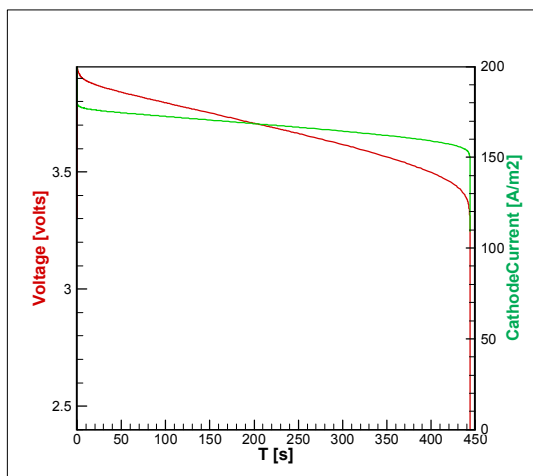
## Results

### Model Development

We have expanded the list of electrode objects that can be used with 1DElectrode to include diffusional objects with and without the total arbitrary Lagrangian Eulerian (TALE) capability.

For our thermal model, we have employed a total enthalpy formulation with additions for electrical potential energy that is conservative up to numerical round-off. All energy loss mechanisms are clearly delineated within this formulation, and analogies to the thermoelectric modeling equations are evident.

We have added the capability to employ arbitrary fitted OCV curves into the electrode object (which is the industry norm) in order to compare against dualfoil, which uses this method exclusively. In contrast, the default method for specification of the OCV within 1DElectrode is to calculate the OCV from the specification of the electrochemical potentials of all of the species involved in the interfacial kinetics reaction, and this is the method that will eventually lead to the greatest progress in understanding degradation methods.



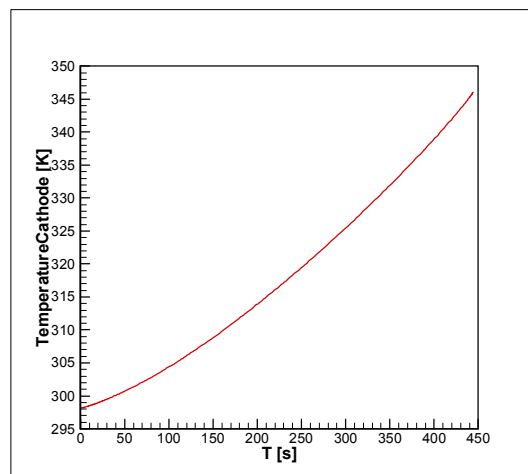
**Figure 1a: Comparisons of high current cantrilbat calculations against Mao et al., using the OCV fitting capability, the generalized Butler-Volmer implementation, and Surface Damkoeler limiter within Cantera.**

We have added to Cantera the ability to combine the concepts of a generalized Butler-Volmer formulation for charge-transfer reactions at interfaces with an affinity formulation, which is used extensively in the geochemistry community and which with the addition of the voltage-dependent modification of the activity energy can be made to look like a generalization of the B-V reaction. We have also added a Damkoeler limiter to

Cantera that has been successful in resolving numerical difficulties in high-current simulations.

### Comparison to High Discharge DualFoil Cases

In order to validate our thermal model we have carried out a validation exercise against dualfoil. We used the simulation of temperature rise problems from Mao et al.<sup>1</sup> Fig. 1 demonstrates that we can duplicate dualfoil calculations fairly well when the problem statement is specified. The work pointed out that additional numerical issues remain within our operator splitting approach that need to be worked out.



**Figure 2b: Corresponding Cathode Temperature vs. time. Temperatures were relatively flat across cell structure**

### CAEBAT development

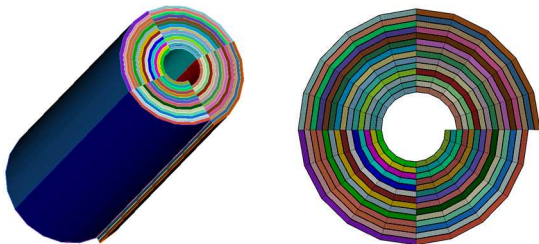
One of the primary tasks has been to integrate the 1D electrode model based on Cantera into Virtual Integrated Battery Environment (VIBE). We have successfully integrated this new software into the suite of components for modeling electro-chemistry inside VIBE. Below we show an existing example to demonstrate the capability to swap the dualfoil with the 1D electrode component and perform a coupled electrochemical, electrical and thermal simulation. In FY15, we have performed some detailed validation and comparison of the cell level simulations.

### Example: Cylindrical Cell (Electrochemical-Electrical-Thermal)

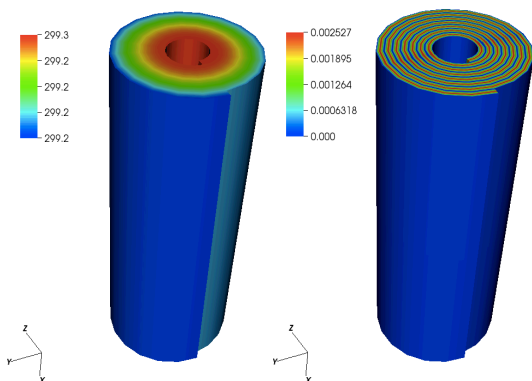
This example contains the electro-chemistry, electrical and thermal transport components in a rolled cylindrical

<sup>1</sup> Mao et al., J. Power Sources, 271 (2014) p. 444.

cell. Fig. 2a shows the geometry and the finite element mesh used to resolve the geometry of the cylindrical cell and the current collectors. The top hierarchy model has 168 (56 each for the cell-sandwich and positive and negative current collectors) zones in 4 quadrants. The zones describe different current collector and cell sandwich regions. The simulation uses 56 concurrent 1D Electrode simulations for different cell-sandwich zones. Typical results are shown in Fig. 2b. The maximum temperature occurs at the cell core as expected.



**Figure 2a: Geometry and mesh of the simulated cylindrical cell**



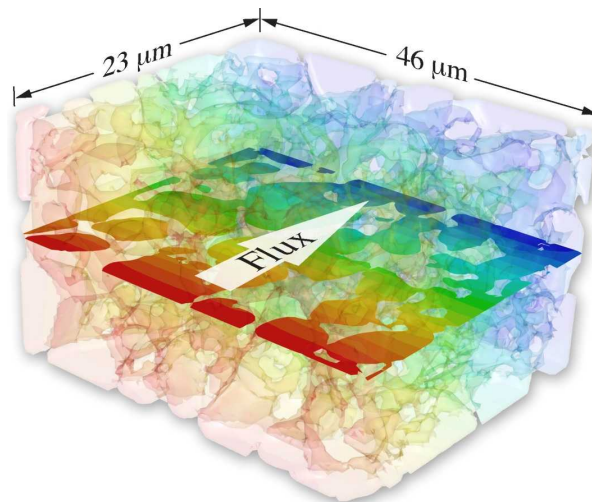
**Figure 2b: Sample results for cylindrical cell (temperature on the left and the electrical potential on the right)**

#### Effective Properties from microscale electrode calculations

The CSM team has reconstructed Li-ion battery cathodes from Focused-Ion-Beam—Scanning Electron Microscope (FIB-SEM) experiments. The three-dimensional reconstructions form the geometrical basis for detailed transport and electrochemistry modeling. The models are implemented using User-Defined Function (UDF) interfaces to the ANSYS FLUENT software. An important aspect of the research is to upscale effective macroscopic properties from the detailed microscale reconstructions.

Effective mass density and specific heat capacity can be evaluated in a straightforward manner using volume-weighted averages of the intrinsic material properties. The effective thermal conductivity can be derived from modeling heat flux through a reconstructed microstructural cube (cf., Fig. 3). Although the simulation is geometrically complex, the thermal transport model is linear and easily accomplished with FLUENT.

The effective conductivity is evaluated in terms of the modeled flux and the overall microscale cube dimensions.



**Figure 3: Simulated transport through a reconstructed composite cathode**

Microstructurally derived effective properties can be used in modeling full cells. Fig. 4 shows two illustrative results from modeling an 18650 cell with an internal short. The result on the left-hand side uses average isotropic properties that are derived from electrode microstructures and current-collection foils. The result on the right-hand side uses isotropic microstructurally derived electrode properties, but considers the inherent anisotropy associated with the current-collection foils and the jelly-roll architecture. The anisotropic result shows axial and circumferential heat spreading that is significantly elongated compared to the isotropic model.

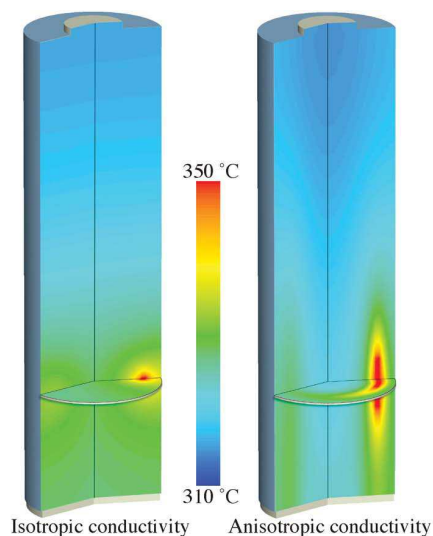
Although evaluating effective properties from microscale reconstructions is relatively straightforward, evaluating effective heat-release rates is much more complicated. The local Faradaic and Ohmic heat release rates can be modeled at the microscale, upscaling to a full cell is difficult. Because the heat-release rates depend strongly on local temperatures and charge/discharge rates, the boundary conditions for the microscale models must have some knowledge of the local conditions within the full cell. In other words, unlike the physical property evaluation, there is a strong coupling between the microscale and macroscale models. Clearly, modeling the microscale behavior within the full battery far exceeds any known computational resources.

#### Microstructurally Derived Heat-Generation Tables

A possible approach for upscaling microstructural heat release rates is being explored, but certainly not complete. Fig. 5 illustrates the general tabular-based idea. The microscale thermal model can be run using a specified charge/discharge rate (C-rate), state of charge (SOC), and isothermal temperature and adiabatic boundary conditions. The result produces the net heat-release rate for the microcube. Such simulations can be precomputed and tabulated for ranges of temperature, SOC, and C-rate.



Based on the local conditions, the macroscale model evaluates heat-release rates from the table

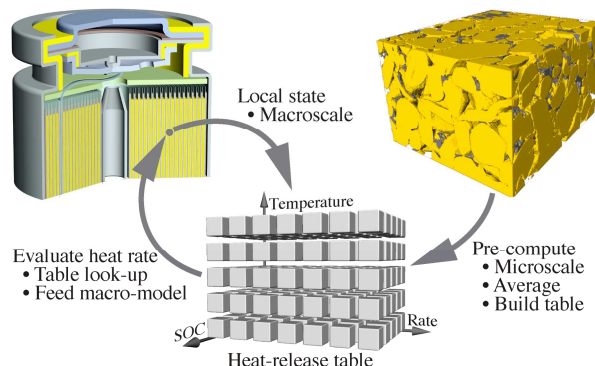


**Figure 4: Simulated thermal response from an internal short in an 18650 cell**

Although the tabular approach works in principle, the practicality is unclear. Simply populating the table from detailed three-dimensional microscale models is computationally intensive (order of months). And, new tables would be needed for each battery electrode of interest. As battery technology evolves, manufacturers frequently implement new and improved architectures. So, the microscale modeling process must begin by developing the FIB-SEM or X-ray tomographic reconstructions. Then, the heat-release models must be run and tabulated. Deriving the needed physical properties is certainly realistic. However, the computational cost for developing the heat release tables is likely impractical.

As a practical matter, local heat-release models at the macroscale are more reasonably derived from local Newman-type models, such as the 1Delectrode model developed elsewhere in this project. Models of the three-dimensional microscale reconstructed electrodes would be

used to assist calibrating and validating the 1Delectrode objects for particular battery and electrode architectures.



**Figure 5: Methods of upscaling of heat generation tables are being evaluated**

## Conclusions and Future Directions

In addition to the partially saturated porous flow and solid mechanics modeling efforts which we have planned, we have started to design new models for the SEI layers based on analogs to corrosion system, whose formulation reactions are thermodynamically reversible, so that they may be designed to dissipate under some conditions. Combining these models with traditional thermal models for thermal runaway, we will then attempt to fit these against Sandia's Batlab data.

## FY 2014-15 Publications/Presentations

1. 2015 DOE Annual Peer Review Meeting Presentation
2. 89th Lithium Battery Technical/Safety Group Meeting, Sandia Labs, Sept 2014.
3. J. Hewson, H Moffat, V. Brunini, Mario Martinez, R. Muller, CantrilBat - 1D Modeling of Batteries, Sandia Report, Albuquerque, NM in prep (2016)